

Semiempirical Extended Hartree-Fock Theory

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Received September 18, 1972

A truncated multi-configuration SCF formalism is presented which is particularly suited to describe correlation effects in semiempirical molecular orbital methods. The orbital energies reflect a correlated, SCF-like description of the situation of electrons in molecules. On the basis of symmetrically orthogonalized atomic orbitals approximations are introduced which lead to CNDO and INDO like methods. Consistency requirements lead to a new formula for the β integral. The method can be parametrized so as to yield good ground state potential surfaces. The orbital part is demonstrated in the simple case of H_2 .

Key words: Semiempirical MO theory – Multiconfiguration SCF formalism

1. Introduction

Semiempirical molecular orbital methods have a great deal of attraction among chemists these days. However, to our knowledge, there exists presently no semiempirical method which includes correlation effects in a theoretically satisfactory and practically useful fashion. CNDO and INDO methods were designed by Pople and collaborators [1] to reproduce dipole moments and equilibrium geometries, but fail to predict binding energies and force constants [2]. Since the binding energies are in general too large, it would be meaningless to add a configuration interaction formalism to the existing scheme. Dewar and collaborators have designed a sequence of MINDO methods and managed after extensive use of adjustable empirical parameters to obtain both equilibrium distances and binding energies [3]. Both methods are based on the SCF formalism and thus unable to describe potential surfaces far from the equilibrium.

We propose here a procedure which allows with little empirical adjustment to retain the attractive features of both Pople's and Dewar's work, namely to be theoretically justifiable and practically useful. For this purpose we develop a modified and truncated multi-configuration SCF formalism. In this formalism we introduce systematic approximations by means of a symmetrically orthogonalized AO basis [4]. Various levels of ZDO assumptions lead to CNDO and INDO like methods. The consequences of the ZDO assumption are reflected in the representation of formulas of the remaining integrals. In particular, a new formula for the β integral is derived which reduces the number of adjustable parameters considerably.

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The definition of a multi-configuration SCF operator after a CI step yields orbital energies which are physically more meaningful than SCF energies, in particular, at distances far from the equilibrium. This is demonstrated for the simple case of H_2 . For polyatomics the use of a localization procedure is suggested to reduce the number of configurations for dissociation. The involved relation to the orbital picture is briefly discussed.

2. The Extended Hartree-Fock Method

In our discussion of correlation effects, we restrict ourselves to intra-shell pair correlation. The total wavefunction is approximated as a linear combination of the dominant Hartree-Fock configuration Ψ_0 and doubly excited configurations Ψ_i of closed-shell or open-shell form.

$$\Psi = A_0 \Psi_0 + \sum_{i=1}^I A_i \Psi_i \quad (2.1)$$

with

$$\Psi_0 = (\psi_1 \bar{\psi}_1 \psi_2 \bar{\psi}_2 \dots \psi_k \bar{\psi}_k \dots \psi_n \bar{\psi}_n),$$

$$\Psi_i = \begin{cases} (\psi_1 \bar{\psi}_1 \psi_2 \bar{\psi}_2 \dots \psi_p \bar{\psi}_p \dots \psi_n \bar{\psi}_n) & \text{closed shell} \\ \frac{1}{\sqrt{2}} [(\psi_1 \bar{\psi}_1 \psi_2 \bar{\psi}_2 \dots \psi_p \bar{\psi}_q \dots \psi_n \bar{\psi}_n) & \text{open shell} \\ -(\psi_1 \bar{\psi}_1 \psi_2 \bar{\psi}_2 \dots \bar{\psi}_p \psi_q \dots \psi_n \bar{\psi}_n)] \end{cases}$$

$$1 \leq k \leq n; p, q > n.$$

For convenience, we use the abbreviation i for (k, p) or (kk, pq) . The set $\Psi_0, \Psi_i (i=1 \dots I)$ is orthonormal. Usually the multiconfiguration Hartree-Fock equations [5, 6] are derived by a variation of the following energy functional with respect to the MO's ψ subject to the orthogonality conditions.

$$E = \langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle \quad (2.2)$$

$$= \left(A_0^2 H_{00} + 2 \sum_{i=1}^I A_0 A_i H_{0i} + \sum_{i,j} A_i A_j H_{ij} \right) / \left(A_0^2 + \sum_{i=1}^I A_i^2 \right)$$

with

$$H_{ij} = \langle \Psi_i | H | \Psi_j \rangle$$

The coefficients A are determined by a secular equation.

$$\sum_{j=0}^I A_j (H_{ij} - E \delta_{ij}) = 0, \quad i = 0, 1 \dots I \quad (2.3)$$

We suggest another way of arriving at (2.3). This will open the way to eigenvalue equations of an extended Hartree-Fock Hamiltonian which appears to be particularly useful in semiempirical methods. We shall show later that the resulting eigenvalues can be physically interpreted.

If we consider the exact eigenfunctions Ψ of the system's Hamiltonian H , the following equality holds

$$E = \langle \Psi_i | H | \Psi \rangle / \langle \Psi_i | \Psi \rangle, \quad i = 0, 1, \dots$$

With (2.1) the energy takes the form

$$E = H_{ii} + \sum_{j \neq i} a_j H_{ij}, \quad i = 0, 1, \dots \quad (2.4)$$

with

$$a_j = A_j / A_i.$$

Concerning the determination of coefficient A_i and energy E , (2.4) is equivalent to (2.3) also in a finite expansion. In particular the total energy of the ground state is represented as a sum of Hartree-Fock energy and correlation energy in a simple form.

$$E = H_{00} + \sum_{i=1} a_i H_{0i} \quad \text{with} \quad a_j = A_j / A_0. \quad (2.4a)$$

Such an expression has also been used by Öksüz and Sinanoglu [7]. The A_i are determined by (2.4). If the molecular orbitals ψ_i used in (2.2) and (2.4) are the same, the ground state energy values of (2.2) and (2.4a) will be the same. However, variation of (2.2) and (2.4a) with respect to the MO's ψ_i leads to different multi-configuration SCF operators, hence to different ψ_i . In general, (2.4) will yield less correlation energy than (2.2) at intermediate internuclear distances. Dissociation is, however, described properly. The advantage of this extended Hartree-Fock operator is the linear form of correlation energy in the A_i which makes the eigenvalues ε_i of such an operator the straightforward generalization of the eigenvalues of an SCF operator. This is not the case for the multiconfiguration orbital energies of Das and Wahl [5] or Veillard and Clementi [6].

In the following, we shall demonstrate the derivation of a multi-configuration closed-shell case. A generalization to open-shells is straightforward. The total energy expressed in integrals over MO's i ($\equiv \psi_i$) is

$$E = 2 \sum_i^n H_{ii}^{\text{core}} + \sum_{i,j}^n 2J_{ij} - K_{ij} + \sum_{k,p} a_{kp} K_{kp}$$

$$H_{ii}^{\text{core}} = \langle i | H_{\text{core}} | i \rangle$$

$$J_{ij} = (ii | jj) \quad (2.5)$$

$$K_{ij} = (ij | ij)$$

$$K_{kp} = (kp | kp)$$

$$a_{kp} = A_{kp} / A_0.$$

MO's k, \bar{k} of Ψ_0 are replaced by p, \bar{p} to form a representative doubly excited configuration. Variation of the energy subject to the MO orthogonality conditions

$$\delta \left(E + \sum_{i,j} \varepsilon_{ij} \langle i | j \rangle \right) = 0$$

yields

$$F_i|i\rangle = \sum_j \varepsilon_{ij}|j\rangle, \quad i=1 \dots n \quad (2.6)$$

with

$$F_i = F_i^{\text{SCF}} + W_i$$

$$W_i = \sum_{l>n} a_{il} W_{il}.$$

We obtain an explicit form for W_{il} in the following way. Since K_{kp} does not depend on ψ_i for $i \neq k$, it holds that

$$W_{il} = W_{kp} \delta_{ik} \delta_{lp}.$$

For $i = k$ K_{kp} can be rewritten as

$$K_{kp} = \frac{1}{2} \langle k(1) | V_{kp} + V_{kp}^\dagger | k(1) \rangle$$

with

$$V_{kp} = \left[k(2) \left| \frac{1}{r_{12}} |p(1)p(2)\rangle \langle k(1)| \right. \right] \quad (2.7)$$

$$V_{kp}^\dagger = \left[|k(1)\rangle \langle p(2)p(1)| \frac{1}{r_{12}} |k(2) \right]$$

so that

$$W_{kp} = \frac{1}{2} (V_{kp} + V_{kp}^\dagger).$$

For the unoccupied SCF orbitals $i = p$ the coupling operator W_{pk} is obtained by exchange of k and p in (2.7). Also $a_{pk} = a_{kp}^{-1}$ holds. The coupling part of the Hamiltonian then takes the final form

$$W_i = \begin{cases} 0 & i = 1 \dots n, i \neq k, \\ \sum_p a_{kp} W_{kp} & \text{for } i = k, \\ \sum_k a_{kp}^{-1} W_{pk} & i = p, p > n. \end{cases} \quad (2.8)$$

Because of the difference between (2.2) and (2.4) the coupling operator W is only half of the one in Wahl's paper [5]. A similar form to (2.8) appears in Kutzelnigg's approximate natural orbital approach [8].

The non-diagonal Lagrangean multipliers ε_{ij} can be absorbed by the use of orthogonality relations [5]. The final equations then take the form

$$(F_i - R_i)|i\rangle = \varepsilon_i|i\rangle \quad (2.9)$$

$$R_i = \sum_{j \neq i} |j\rangle \langle j| F_i + F_i |j\rangle \langle j|.$$

In practice, one cycle of the following three steps will be sufficient to obtain an improved SCF-like description: 1) Solution of the SCF equations, 2) Determination of the CI coefficients A by means of (2.3), 3) Solution of the EHF equations (2.9). Repetition of this cycle will not lead to new aspects, but may involve

convergence problems, so we do not advocate it here. The energy can then be written in the following way

$$\begin{aligned}
 E &= \sum_i^n \langle i | H_{\text{core}} + F_i | i \rangle \\
 &= \sum_i^n \langle i | H_{\text{core}} + F_i^{\text{SCF}} + W_i | i \rangle \\
 &= \sum_i^n (\varepsilon_i^{\text{core}} + \varepsilon_i).
 \end{aligned} \tag{2.10}$$

The orbital energies play here the same role as in SCF theory, but include correlation effects.

3. CNDO and INDO Forms

To relate the formalism of Section 2 to approximate molecular orbital methods, we expand the MO's in AO's and write the EHF equations in matrix form

$$\begin{aligned}
 (F_i - R_i)C_i &= \varepsilon_i C_i \quad i = 1 \dots n, \dots, p \dots \\
 F_i &= F_i^{\text{SCF}} + W_i \\
 R_i &= \sum_j (S C_j C_j^\dagger F_i + F_i C_j C_j^\dagger S).
 \end{aligned} \tag{3.1}$$

We concentrate now on the representative operator F_k . Its elements are

$$F_{\mu\nu} = F_{\mu\nu}^{\text{SCF}} + W_{\mu\nu}$$

with

$$\begin{aligned}
 F_{\mu\nu}^{\text{SCF}} &= H_{\mu\nu}^{\text{core}} + \sum_{\varrho, \sigma} P_{\varrho\sigma} [(\mu\nu | \varrho\sigma) - \frac{1}{2}(\mu\varrho | \nu\sigma)] \\
 W_{\mu\nu} &= \frac{1}{2} \sum_{\varrho, \sigma} \sum_{\tau, \omega} P'_{\varrho\sigma} P''_{\tau\omega} [(\mu\tau | \varrho\omega) S_{\sigma\nu} + (\nu\tau | \varrho\omega) S_{\sigma\mu}] \\
 P_{\varrho\sigma} &= 2 \sum_i^{\text{occ}} c_{i\varrho} c_{i\sigma} = 2 \sum_i^{\text{occ}} P_{\varrho\sigma}(i) \\
 P'_{\varrho\sigma} &= c_{k\varrho} c_{k\sigma} \\
 P''_{\tau\omega} &= \sum_p c_{p\tau} c_{p\omega} a_{kp}.
 \end{aligned} \tag{3.2}$$

In the following symmetrically orthogonalized AO's [4] will be assumed, which lead to further simplifications

$$\begin{aligned}
 R_i &= \sum_j C_j C_j^\dagger F_i + F_i C_j C_j^\dagger \\
 W_{\mu\nu} &= \frac{1}{2} \sum_{\varrho} \sum_{\tau, \omega} P''_{\tau\omega} [P'_{\varrho\nu}(\mu\tau | \varrho\omega) + P'_{\varrho\mu}(\nu\tau | \varrho\omega)].
 \end{aligned} \tag{3.3}$$

Various levels of approximation will be considered:

a) CNDO form

$$\begin{aligned}
 F_{\mu\mu}^{\text{SCF}} &= H_{\mu\mu}^{\text{core}} + \frac{1}{2}P_{\mu\mu}(\mu\mu|\mu\mu) + \sum_{\varrho \neq \mu} P_{\varrho\varrho}(\mu\mu|\varrho\varrho) \\
 F_{\mu\nu}^{\text{SCF}} &= H_{\mu\nu}^{\text{core}} - \frac{1}{2}P_{\mu\nu}(\mu\mu|\nu\nu) \\
 W_{\mu\mu} &= \sum_{\varrho} P'_{\varrho\mu} P''_{\varrho\mu}(\mu\mu|\varrho\varrho) \\
 W_{\mu\nu} &= \frac{1}{2} \sum_{\varrho} P'_{\varrho\nu} P''_{\varrho\mu}(\mu\mu|\varrho\varrho) + P'_{\varrho\mu} P''_{\varrho\nu}(\nu\nu|\varrho\varrho)
 \end{aligned} \tag{3.4}$$

so that

$$\begin{aligned}
 F_{\mu\mu} &= H_{\mu\mu}^{\text{core}} + \frac{1}{2}(P_{\mu\mu} + 2P'_{\mu\mu} P''_{\mu\mu})(\mu\mu|\mu\mu) \\
 &\quad + \sum_{\varrho \neq \mu} (P_{\varrho\varrho} + P'_{\varrho\mu} P''_{\varrho\mu})(\mu\mu|\varrho\varrho) \\
 F_{\mu\nu} &= H_{\mu\nu}^{\text{core}} - \frac{1}{2}[P_{\mu\nu} - (P'_{\mu\mu} + P'_{\nu\nu})P''_{\mu\nu}](\mu\mu|\nu\nu) \\
 &\quad + \frac{1}{2}P'_{\mu\nu}(P''_{\mu\mu} + P''_{\nu\nu})(\mu\mu|\mu\mu) \\
 &\quad + \frac{1}{2} \sum_{\varrho \neq \mu, \nu} P'_{\varrho\nu} P''_{\varrho\mu}(\mu\mu|\varrho\varrho) + P'_{\varrho\mu} P''_{\varrho\nu}(\nu\nu|\varrho\varrho).
 \end{aligned} \tag{3.5}$$

It is widely believed that semiempirical SCF methods can account for correlation by empirical adjustment of parameters. How much of this is true will be shown in the following. We try to reduce the EHF equations (3.5) to an SCF form:

$$F_{\mu\mu} = H_{\mu\mu}^{\text{core}} + \frac{1}{2}P_{\mu\mu}(\mu\mu|\mu\mu)' + \sum_{\varrho \neq \mu} P_{\varrho\varrho}(\mu\mu|\varrho\varrho)'$$

with

$$(\mu\mu|\mu\mu)' = \left(1 + 2 \frac{P'_{\mu\mu} P''_{\mu\mu}}{P_{\mu\mu}}\right) (\mu\mu|\mu\mu) \tag{3.6a}$$

$$(\mu\mu|\varrho\varrho)' = \left(1 + \frac{P'_{\varrho\mu} P''_{\varrho\mu}}{P_{\mu\mu}}\right) (\mu\mu|\varrho\varrho)$$

$$F_{\mu\nu} = H_{\mu\nu}^{\text{core}} - \frac{1}{2}P_{\mu\nu}(\mu\mu|\nu\nu)' + \Delta_{\mu\nu}$$

with

$$(\mu\mu|\nu\nu)' = \left(1 - \frac{(P'_{\mu\mu} + P'_{\nu\nu})P''_{\mu\nu}}{P_{\mu\nu}}\right) (\mu\mu|\nu\nu) \tag{3.6b}$$

$$\Delta_{\mu\nu} = \frac{1}{2}P'_{\mu\nu}(P''_{\mu\mu} + P''_{\nu\nu})(\mu\mu|\mu\mu)$$

$$+ \frac{1}{2} \sum_{\varrho \neq \mu, \nu} P'_{\varrho\nu} P''_{\varrho\mu}(\mu\mu|\varrho\varrho) + P'_{\varrho\mu} P''_{\varrho\nu}(\nu\nu|\varrho\varrho).$$

From (3.6a) it appears that modified one- and two-center repulsion integrals could be introduced which would keep the SCF formalism intact. However, (3.6b) shows that the modifications to be introduced here are not consistent with those in (3.6a). Also a new term $\Delta_{\mu\nu}$ appears which has no analogue in SCF theory. It is hard to conceive that the modifications for parametrization introduced in (3.6) would be satisfactory even under further simplifying assumptions in a particular class of molecules with fixed geometries. It is obvious from there that previous attempts of reparametrization had to fail [9, 10]. Caution was expressed already in Hansen's paper.

Equations (3.5) involve only four types of parameters

$$\alpha_\mu \equiv H_{\mu\mu}^{\text{core}}, \beta_{\mu\nu} \equiv H_{\mu\nu}^{\text{core}}, (\mu\mu|\mu\mu), (\mu\mu|\nu\nu),$$

whose evaluation will now be attempted. In the calculation of α we follow Pople

with

$$\alpha_\mu = W_\mu - \sum_{B \neq A} U_{AB}$$

$$U_{AB} = \begin{cases} \int s_A^2(1) \frac{Z_B}{r_{1B}} d\tau_1 & \text{CNDO/1} \\ Z_B \gamma_{AB} & \text{CNDO/2.} \end{cases} \quad (3.7)$$

It should be noticed here that in the choice of W_μ ($W_s \neq W_p$) Pople does not (!) follow his invariance requirements. He drops the invariance under hybridization. But this is not serious, since recent work shows [11, 12] that invariance under hybridization is not a necessary, but sufficient condition for the invariance of the SCF equations.

To evaluate β , we use our own studies. We have shown that in polyatomics [13, 14]

$$\bar{\beta}_{\mu\nu} = \frac{1}{2} S_{\mu\nu} [(\bar{\alpha}_\mu + \bar{\alpha}_\nu) + \kappa_{\mu\nu}(\bar{\alpha}_\mu - \bar{\alpha}_\nu)] + \frac{1 - S_{\mu\nu}^2}{R_{\mu\nu}} \frac{dS_{\mu\nu}}{dR_{\mu\nu}} \quad (3.8)$$

and in diatomics [15]

$$\beta_{\mu\nu} = \frac{1}{1 - S_{\mu\nu}^2} \left[\bar{\beta}_{\mu\nu} - \frac{1}{2} S_{\mu\nu} (\bar{\alpha}_\mu + \bar{\alpha}_\nu) \right] \quad (3.9)$$

holds.

The simplest approximation for the two-center integral β_{ab} better than Linderberg's [16], which was proven to be unreliable [13], would then be

$$\begin{aligned} \beta_{ab} &\approx \frac{1}{2} S_{ab} [(\bar{\alpha}'_a + \bar{\alpha}'_b) + \kappa_{ab}(\bar{\alpha}'_a - \bar{\alpha}'_b)] + \frac{1}{R} \frac{dS_{ab}}{dR} - \frac{1}{2} S_{ab} (\bar{\alpha}_a + \bar{\alpha}_b) \\ &= \frac{1}{2} S_{ab} [(\Delta\bar{\alpha}_a + \Delta\bar{\alpha}_b) + \kappa_{ab}(\bar{\alpha}_a - \bar{\alpha}_b + \Delta\bar{\alpha}_a - \Delta\bar{\alpha}_b)] + \frac{1}{R} \frac{dS_{ab}}{dR}. \end{aligned} \quad (3.10)$$

In the spirit of the CNDO method we put

$$\Delta\bar{\alpha}_a + \Delta\bar{\alpha}_b = -\Delta Z \gamma_{AB} \quad (3.11)$$

with

$$\Delta Z = Z'_A - Z_A + Z'_B - Z_B.$$

ΔZ can be used as an adjustable parameter, e.g. to adjust the binding energy.

Since it is well known that the electronic Coulomb integrals over orthogonalized orbitals do not differ considerably from their non-orthogonal counterparts, we again follow Pople to put

$$\gamma_{AA} = (\mu_A \mu_A | \mu_A \mu_A) = (\mu_A \mu_A | v_A v_A) = (s_A s_A | s_A s_A) \quad (3.12)$$

$$\gamma_{AB} = (\mu_A \mu_A | \sigma_B \sigma_B) = (s_A s_A | s_B s_B).$$

The total energy including nuclear repulsion can be separated in "atomic" and "interatomic" parts.

$$\begin{aligned} E &= \sum_A (E_A^{\text{SCF}} + E_A^{\text{corr}}) + \sum_{A < B} (E_{AB}^{\text{SCF}} + E_{AB}^{\text{corr}}) \\ E_A^{\text{SCF}} &= \sum_{\mu}^A P_{\mu\mu} W_{\mu} + \frac{1}{2} \sum_{\mu, \nu}^A (P_{\mu\mu} P_{\nu\nu} - \frac{1}{2} P_{\mu\nu}^2) \gamma_{AA} \\ E_{AB}^{\text{SCF}} &= \sum_{\mu}^A \sum_{\nu}^B (2P_{\mu\nu} \beta_{\mu\nu} - \frac{1}{2} P_{\mu\nu}^2 \gamma_{AB}) \\ &\quad + Z_A Z_B R_{AB}^{-1} - P_{AA} U_{AB} - P_{BB} U_{BA} + P_{AA} P_{BB} \gamma_{AB} \quad (3.13) \\ E_A^{\text{corr}} &= [\frac{1}{2} \sum_k \sum_{\mu}^A \sum_{\nu}^A \sum_{\rho}^A P_{\mu\nu}(k) P'_{\rho\nu}(k) P''_{\rho\mu}(k)] \gamma_{AA} \\ E_{AB}^{\text{corr}} &= [\sum_k \sum_{\mu}^A \sum_{\nu}^B \sum_{\rho}^B P_{\mu\nu}(k) P'_{\rho\nu}(k) P''_{\rho\mu}(k)] \gamma_{AB}. \end{aligned}$$

b) INDO forms

$$\begin{aligned} F_{\mu\mu}^{\text{SCF}} &= F_{\mu\mu}^{\text{SCF, CNDO}} - \frac{1}{2} \sum_{\rho \neq \mu}^{A\mu} P_{\rho\rho} (\mu\rho | \mu\rho) \\ F_{\mu\nu}^{\text{SCF}} &= F_{\mu\nu}^{\text{SCF, CNDO}} - \frac{3}{2} P_{\mu\nu} (\mu\nu | \mu\nu) \delta_{A_{\mu} A_{\nu}} \\ W_{\mu\mu} &= W_{\mu\mu}^{\text{CNDO}} + \sum_{\rho \neq \mu}^A (P'_{\mu\mu} P''_{\rho\rho} + P'_{\rho\mu} P''_{\rho\mu}) (\mu\rho | \mu\rho) \quad (3.14) \\ W_{\mu\nu} &= W_{\mu\nu}^{\text{CNDO}} + \frac{1}{2} \sum_{\rho}^{A\mu} (P'_{\mu\nu} P''_{\rho\rho} + P'_{\rho\nu} P''_{\rho\mu}) (\mu\rho | \mu\rho) \\ &\quad + \frac{1}{2} \sum_{\rho}^{A\nu} (P'_{\mu\nu} P''_{\rho\rho} + P'_{\rho\mu} P''_{\rho\nu}) (\nu\rho | \nu\rho) \end{aligned}$$

so that

$$\begin{aligned}
 F_{\mu\mu} &= F_{\mu\mu}^{\text{CNDO}} + \sum_{\substack{\Lambda\mu \\ \varrho \neq \mu}}^{\Lambda\mu} (P'_{\mu\mu} P''_{\varrho\varrho} + P'_{\varrho\mu} P''_{\varrho\mu} - \frac{1}{2} P_{\varrho\varrho}) (\mu\varrho | \mu\varrho) \\
 F_{\mu\nu} &= F_{\mu\nu}^{\text{CNDO}} - \frac{3}{2} P_{\mu\nu} (\mu\nu | \mu\nu) \delta_{\Lambda\mu\Lambda\nu} \\
 &\quad + \frac{1}{2} \sum_{\substack{\Lambda\mu \\ \varrho \neq \mu}}^{\Lambda\mu} (P'_{\mu\nu} P''_{\varrho\varrho} + P'_{\varrho\nu} P''_{\varrho\mu}) (\mu\varrho | \mu\varrho) \\
 &\quad + \frac{1}{2} \sum_{\substack{\Lambda\nu \\ \varrho \neq \nu}}^{\Lambda\nu} (P'_{\mu\nu} P''_{\varrho\varrho} + P'_{\varrho\mu} P''_{\varrho\nu}) (\nu\varrho | \nu\varrho).
 \end{aligned} \tag{3.15}$$

In addition to the CNDO parameters, exchange integrals appear. For the same reasons as in the CNDO part, all two-electron integrals are evaluated over non-orthogonal orbitals according to Pople's procedure. Differences arise in the evaluation of $\alpha_\mu \equiv H_{\mu\mu}^{\text{core}}$ and $\beta_{\mu\nu} \equiv H_{\mu\nu}^{\text{core}}$. We have shown previously [15] that in diatomics

$$\alpha_\mu = \frac{1}{1 - S_{\mu\nu}^2} \left[\bar{\alpha}_\mu - \frac{1}{2} (1 - \sqrt{1 - S_{\mu\nu}^2}) (\bar{\alpha}_\mu - \bar{\alpha}_\nu) - S_{\mu\nu} \bar{\beta}_{\mu\nu} \right] \tag{3.16}$$

holds. A combination of (3.16) with (3.8) yields

$$\alpha_a = \bar{\alpha}_a - \frac{1}{2} \frac{(1 - \sqrt{1 - S_{ab}^2}) - (1 - \kappa_{ab}^2)}{1 - S_{ab}^2} (\bar{\alpha}_a - \bar{\alpha}_b) - \frac{S_{ab}}{R} \frac{dS_{ab}}{dR}. \tag{3.17}$$

In the CNDO method Pople neglected the second and third term in (3.17) and we followed in (3.7) to keep in line with the CNDO invariance assumptions. In the INDO method however, the neglect of these terms cannot be justified.

To obtain a valid formula for β_{ab} , we use again (3.10), but replace (3.11) by

$$\Delta \bar{\alpha}_a = K_a \bar{\alpha}_a. \tag{3.18}$$

K is considered as an adjustment parameter. The total energy is again separated in atomic and interatomic, SCF and correlation part

$$E = \sum_A (E_A^{\text{SCF}} + E_A^{\text{corr}}) + \sum_{A < B} (E_{AB}^{\text{SCF}} + E_{AB}^{\text{corr}}). \tag{3.19}$$

For reasons of convenience, we do not list the detailed expressions, they can be obtained similarly to the CNDO approach. Differences will not only arise through the appearance of exchange integrals, but also through modification of α 's and β 's.

4. Orbital Description of the Ground State of H_2

To demonstrate the consequences of the foregoing sections, we choose the simple example of the ground state of H_2 . Let us take, for convenience, a double configuration wavefunction which allows for proper dissociation.

$$\Psi = A_0 \Psi_0 + A_1 \Psi_1 \tag{4.1}$$

with

$$\begin{aligned}\Psi_0 &= 1s\sigma_g(1)1s\sigma_g(2) \\ \Psi_1 &= 1s\sigma_\mu(1)1s\sigma_\mu(2).\end{aligned}$$

The first term represents the Hartree-Fock part, the second the correlation part. We now approximate the MO's as a linear combination of symmetrically orthogonalized AO's a, b

$$\begin{aligned}1s\sigma_g &= \frac{1}{\sqrt{2}}(a+b) \\ 1s\sigma_\mu &= \frac{1}{\sqrt{2}}(a-b).\end{aligned}\tag{4.2}$$

Under neglect of differential overlap the elements of the EHF operator take the form

$$\begin{aligned}F_{aa}^{\text{EHF}} &= \alpha_a + \frac{1}{2}\left(1 + \frac{1}{2}\frac{A_1}{A_0}\right)(aa|aa) + \left(1 - \frac{1}{4}\frac{A_1}{A_0}\right)(aa|bb) \\ F_{ab}^{\text{EHF}} &= \beta_{ab} + \frac{1}{4}\frac{A_1}{A_0}(aa|aa) - \frac{1}{2}\left(1 + \frac{1}{2}\frac{A_1}{A_0}\right)(aa|bb).\end{aligned}\tag{4.3}$$

For $A_1 = 0$ we obtain the well-known Hartree-Fock elements

$$\begin{aligned}F_{aa}^{\text{SCF}} &= \alpha_a + \frac{1}{2}(aa|aa) + (aa|bb) \\ F_{ab}^{\text{SCF}} &= \beta_{ab} - \frac{1}{2}(aa|bb).\end{aligned}\tag{4.4}$$

If we wish to reduce the diagonal part of the EHF operator to SCF form, we can put

$$\begin{aligned}(aa|aa)' &= \left(1 + \frac{1}{2}\frac{A_1}{A_0}\right)(aa|aa) \\ (aa|bb)' &= \left(1 - \frac{1}{4}\frac{A_1}{A_0}\right)(aa|bb).\end{aligned}$$

A_1/A_0 is negative, as can be seen from the secular equation

$$\begin{aligned}\frac{A_1}{A_0} &= -\frac{H_{00} - E}{H_{01}} \\ H_{00} &> E, \quad H_{01} > 0.\end{aligned}\tag{4.5}$$

This implies that the single-center repulsion integral is decreased, whereas the two-center integral is increased. The maximum change occurs for large internuclear distances where $A_1/A_0 \rightarrow -1$ and amounts to 50% decrease for the single-center integral and 25% increase for the two-center integral. Unfortunately, this parametrization cannot be applied to F_{ab}^{EHF} . Here, $(aa|bb)'$ must equal $\left(1 + \frac{1}{2}\frac{A_1}{A_0}\right)$ and an entirely new term $(aa|aa)$ appears. We conclude that it is impossible to define modified one- and two-center integrals consistently for both diagonal and non-diagonal elements of the EHF operator.

We now proceed to the orbital eigenvalues. From symmetry reason, the MO's σ_g and σ_u are orthogonal. So the orthogonalization operator R can be dropped. Since the AO's are also orthogonal, we obtain

$$\begin{aligned}\varepsilon_+^{\text{EHF}} &= F_{aa}^{\text{EHF}} + F_{ab}^{\text{EHF}} \\ &= \alpha_a + \beta_{ab} + \frac{1}{2} \left(1 + \frac{A_1}{A_0} \right) (aa|aa) + \frac{1}{2} \left(1 - \frac{A_1}{A_0} \right) (aa|bb)\end{aligned}\quad (4.6)$$

whereas the Hartree-Fock energy would be

$$\varepsilon_+^{\text{SCF}} = \alpha_a + \beta_{ab} + \frac{1}{2} (aa|aa) + \frac{1}{2} (aa|bb). \quad (4.7)$$

The total energy is in both cases

$$E = \varepsilon_+^{\text{core}} + \varepsilon_+$$

so that

$$\begin{aligned}E^{\text{EHF}} &= 2(\alpha_a + \beta_{ab}) + \frac{1}{2} \left(1 + \frac{A_1}{A_0} \right) (aa|aa) + \frac{1}{2} \left(1 - \frac{A_1}{A_0} \right) (aa|bb) \\ E^{\text{SCF}} &= 2(\alpha_a + \beta_{ab}) + \frac{1}{2} (aa|aa) + \frac{1}{2} (aa|bb).\end{aligned}\quad (4.8)$$

For large internuclear distances as $R \rightarrow \infty$, $A_1 \rightarrow -A_0$, the set of formulas appears as follows

$$\begin{aligned}F_{aa}^{\text{EHF}} &= \alpha_a + \frac{1}{4} (aa|aa) \\ F_{ab}^{\text{EHF}} &= -\frac{1}{4} (aa|aa) \\ \varepsilon_+^{\text{EHF}} &= \alpha_a \\ E^{\text{EHF}} &= 2\alpha_a,\end{aligned}\quad (4.9)$$

$$\begin{aligned}F_{aa}^{\text{SCF}} &= \alpha_a + \frac{1}{2} (aa|aa) \\ F_{ab}^{\text{SCF}} &= 0 \\ \varepsilon_+^{\text{SCF}} &= \alpha_a + \frac{1}{2} (aa|aa) \\ E^{\text{SCF}} &= 2\alpha_a + \frac{1}{2} (aa|aa).\end{aligned}\quad (4.10)$$

Most noticeable is that the EHF formalism does not only yield the correct total energy E but also the correct orbital energy ε . An earlier paper on H_2 by Hansen [9] used a CI formalism and did not give this insight. Finally, Wahl's formalism with a twice as large coupling operator would lead to $\varepsilon_+ \rightarrow \alpha_a - \frac{1}{2} (aa|aa)$ for $R \rightarrow \infty$. So Wahl's orbital energies do not reflect the physical situation.

5. Discussion and Conclusion

In this paper, we have developed an Extended Hartree-Fock formalism suitable for semiempirical molecular orbital methods. The advantage of the fact that the correlation energy is represented linearly in the coefficients A in Eq. (2.4) leads to an SCF like orbital approach reflected in Eq. (2.10) for the total energy. In the case of H_2 we demonstrated that the eigenvalues of the EHF operator have physically interpretable characteristics, in particular they follow dissociation properly. To treat polyatomics efficiently, further assumptions about

the MO's would be necessary. Work now in progress will use Boys' localization procedure [17] to keep the number of configurations in polyatomics as small as possible. This is not only easier, but supported by recent results for CH₄ [18] that, contrary to conclusions by Sinanoglu [19], *intra*-pair correlation in localized orbitals is dominant. There are some questions with the orbital picture when the CI part is based on localized orbitals. The following steps would be necessary to keep as close as possible to the delocalized SCF part: 1) Solution of the SCF equations, 2) Localization of the MO's, 3) Solution of the secular equation, 4) Definition of an EHF operator based on localized MO's, 5) Solution of the EHF equations. In general, this last step will partially delocalize the MO's so that the orbital energies ε will be physically descriptive. In CNDO and INDO like forms with minimal basis sets, left-right and angular correlation can be partially accounted for. But there is no way to include in-out correlation.

We have already applied the new parametrization of β integrals in the CNDO and INDO forms of the theory. Most encouraging results for potential curves and force constants will be published elsewhere [20].

Acknowledgement. I appreciate the hospitality of Prof. H. Preuss during my stay in his institute. I thank Dr. W. Meyer for a discussion about some aspects of the correlation problem.

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